

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 3/39, 3/37, 1/02	A1	(11) International Publication Number: WO 99/42551 (43) International Publication Date: 26 August 1999 (26.08.99)
(21) International Application Number: PCT/US99/02394 (22) International Filing Date: 3 February 1999 (03.02.99) (30) Priority Data: 60/075,383 20 February 1998 (20.02.98) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): CHAPMAN, Benjamin, Edgar [US/US]; 9469 Galecrest Drive, Cincinnati, OH 45231 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: BR, CA, CN, IN, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: BLEACH DETERGENT COMPOSITIONS CONTAINING MODIFIED POLYAMINE POLYMERS (57) Abstract A bleach detergent composition comprising a bleach agent, and a complexed polyamine which comprises a modified polyamine and an anionic species capable of forming a complex with the modified polyamine. The modified polyamine is especially useful as a cotton soil release and dispersant agent. The complexed polyamine is substantially non-reactive with the bleach agent in a wash solution containing the bleach detergent composition. The invention also relates to a process for preparing a bleach detergent composition that contains a bleach agent and a complexed polyamine which is substantially non-reactive with the bleach agent in the wash solution.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BLEACH DETERGENT COMPOSITIONS CONTAINING MODIFIED POLYAMINE POLYMERS

FIELD OF THE INVENTION

The present invention relates to a bleach detergent composition that contains a modified polyamine especially useful as a cotton soil release and dispersant agent, and to processes for making.

BACKGROUND OF THE INVENTION

Various fabric surface modifying agents have been commercialized and are currently used in detergent compositions and fabric softener/antistatic articles and compositions. Examples of surface modifying agents are soil release polymers. Soil release polymers typically comprise an oligomeric or polymeric ester "backbone" and are generally very effective on polyester or other synthetic fabrics where the grease or similar hydrophobic stains form an attached film and are not easily removed in an aqueous laundering process. The soil release polymers have a less dramatic effect on "blended" fabrics, that is, on fabrics that comprise a mixture of cotton and synthetic material, and have little or no effect on cotton articles. Alkoxylated polyamines are heretofore known and have been shown to provide specific cleaning benefits. Examples of alkoxylated polyamines are disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. However, it has been surprisingly discovered that effective soil release agents for cotton articles and dispersants can be prepared from certain modified polyamines. This unexpected result has yielded compositions that can provide soil release benefits for cotton articles that were once available only on synthetic and synthetic-cotton blended fabric.

Typically, if bleaching agents are present, especially peroxygen bleaches which are formulated into both liquid and granular laundry detergent compositions, the formulator must consider the instability of a particular soil dispersant toward the bleach. Many successful dispersants have polyalkyleneamine or polyalkyleneimine backbones which are susceptible to oxidation at the amine functionalities and potentially to breakdown or fragmentation by bleaching agents which may be present. From another view, the interaction of bleaching agents with these polyalkyleneimine-based dispersants depletes the amount of bleach present, therefore affecting the bleaching performance.

Accordingly, there remains a need in the art for bleach compatible, highly effective hydrophobic soil dispersants. Surprisingly, it has been found that certain higher molecular weight polyalkyleneimines when complexed with an anionic species, particularly when

complexed at a pH of from about pH 5 to about pH 10, are compatible with a bleach agent in the bleach detergent composition, and additionally provide hydrophobic soil dispersion.

SUMMARY OF THE INVENTION

The present invention is a bleach detergent composition that comprises a bleach agent, and a complexed polyamine which comprises a modified polyamine and an anionic species capable of forming a complex with the modified polyamine. The modified polyamine is especially useful as a cotton soil release and dispersant agent. The complexed polyamine is less reactive with the bleach agent in a wash solution containing the bleach detergent composition. The invention also relates to a process for preparing a bleach detergent composition that contains a bleach agent and a complexed polyamine which is substantially non-reactive with the bleach agent in the wash solution.

The bleach detergent composition more particularly comprises a peroxygen bleach agent, a complexed polyamine comprising a modified polyamine and an anionic agent capable of forming a complex with the modified polyamine, and adjunct detergent ingredients.

The process of the present invention more particularly comprises the steps of pre-mixing a modified polyamine with an anionic agent, preferably an anionic deterative surfactant, to form a complexed polyamine, and thereafter, adding adjunct detergent ingredients, such as builders and water to form the bleach detergent composition.

All documents cited herein are incorporated herein by reference. All percentages and proportions are on a weight basis unless otherwise indicated.

DETAILED DESCRIPTION OF THE INVENTION

The bleach detergent composition preferably comprises:

- a) at least about 0.01% to about 95%, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a detergent surfactant selected from the group consisting of anionic, nonionic, cationic, zwitterionic, and ampholytic surfactants, and mixtures thereof;
- b) from about 0.05% to about 30%, more preferably from about 0.5% to about 30%, most preferably from about 1% to about 20%, by weight, of a bleach agent;
- c) from about 0.01 to about 10% by weight, of a complexed polyamine, the complexed polyamine comprising a water-soluble alkoxyated polyamine and an anionic deterative surfactant; and
- d) adjunct ingredients selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer agents, dispersants, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage

agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

The Bleach Agent

The bleaching agent preferably is a peroxygen bleaching compound which is capable of yielding hydrogen peroxide in an aqueous liquor. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used, if desired. Preferred peroxygen bleaching compounds include sodium perborate, commercially available in the form of mono-, tri-, and tetra-hydrate, sodium pyrophosphate peroxyhydrate, urea peroxy-hydrate, sodium peroxide, peroxyphthalate and sodium percarbonate. Particularly preferred are sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate. Sodium percarbonate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching liquor. It is believed that such rapid dissolution results in the formation of higher levels of percarboxylic acid and, thus, enhanced surface bleaching performance.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

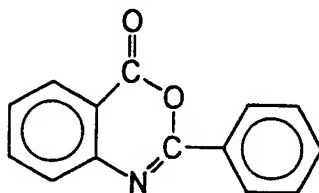
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

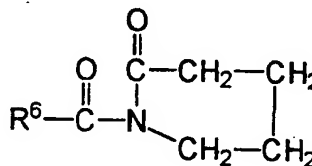
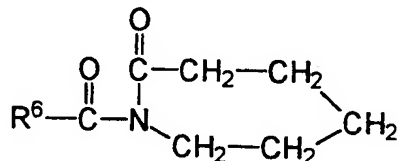
Bleach activators can also be added to the bleach detergent composition in addition to the peroxygen bleaching agents. The peroxygen bleaching agents, the perborates, the

percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:

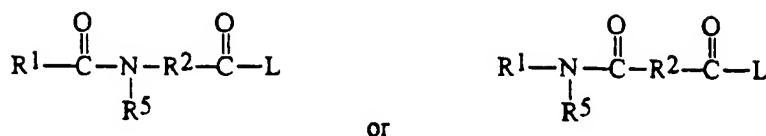


Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Another preferred bleach agent is a peroxyacid bleaching agent, of which an amide substituted peroxyacid precursor compound is more preferred, including one having the formula:



wherein R^1 is C_1 - C_{14} alkyl, aryl, alkylaryl, and mixtures thereof; R^2 is C_1 - C_{14} alkylene, arylene, alkylarylene, and mixtures thereof; R^5 is hydrogen, C_1 - C_{10} alkyl, aryl, alkylaryl, and mixtures thereof; L is any suitable leaving group (a preferred leaving group is phenyl sulfonate). R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may contain, where applicable, branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . The substitution can include alkyl, halogen, nitrogen, sulfur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States

Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

The Modified Polyamine

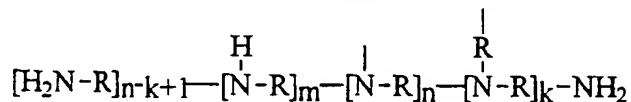
The modified polyamines used in the process invention are water-soluble or water-dispersible, especially useful for cleaning cotton-containing fabrics or as a dispersant. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but preferably substitution is accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the modified polyamines have the general formula:



where the backbones prior to subsequent modification comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones comprising the modified polyamines used in the present invention have the general formula:



where the backbones prior to subsequent modification comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units.

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For

example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

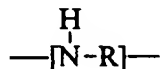


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



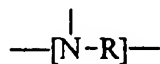
is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



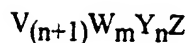
is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

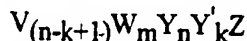


is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

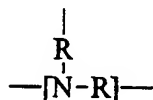
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



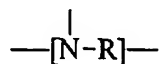
for linear polyamine polymers and by the general formula



for cyclic polyamine polymers. For the case of polyamines comprising rings, a Y' unit of the formula



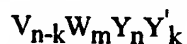
serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

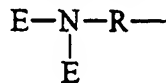


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

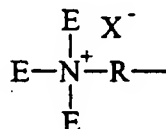
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:

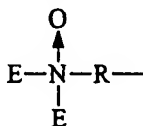


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

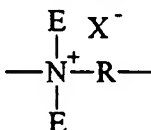


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:

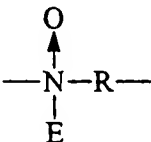


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

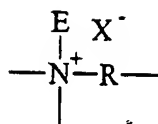


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

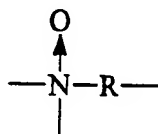


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

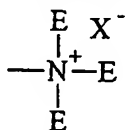


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:

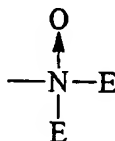


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

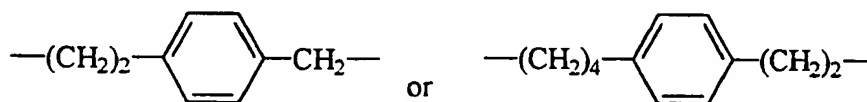
- c) oxidized units having the structure:



When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula $(\text{HOCH}_2\text{CH}_2)\text{HN}-$.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure $-\text{NH}_2$. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₂-C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene.

The "oxy" R units comprise $-(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$,

$-\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}(\text{OR}^2)\text{CH}_2)_w\text{---}$, $-\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{---}$,

$-(\text{R}^1\text{O})_x\text{R}^1\text{---}$, and mixtures thereof. Preferred R units are C₂-C₁₂ alkylene, C₄-C₁₂

alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -

$(\text{R}^1\text{O})_x\text{R}^1\text{---}$, $-\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{---}$, $-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}-$

$(\text{OH})\text{CH}_2)_w\text{---}$, $-(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂

hydroxy-alkylene, C₄-C₁₂ dihydroxyalkylene, $-(\text{R}^1\text{O})_x\text{R}^1\text{---}$, $-(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$,

$-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}-(\text{OH})\text{CH}_2)_w\text{---}$, and mixtures thereof, even more

preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof, most

preferred are C₂-C₆ alkylene. The most preferred backbones of the present invention

comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene. R² is hydrogen, and $-(\text{R}^1\text{O})_xB$, preferably hydrogen.

R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of E units described herein below.

R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈ alkylene, most preferably ethylene or butylene.

R^5 is C_1 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-C(O)(R^4)_rC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, R^5 is preferably ethylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.

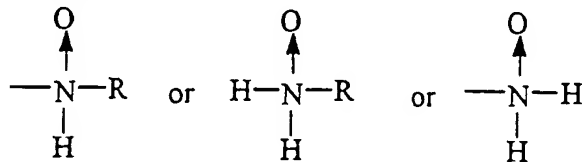
R^6 is C_2 - C_{12} alkylene or C_6 - C_{12} arylene.

The preferred "oxy" R units are further defined in terms of the R^1 , R^2 , and R^5 units. Preferred "oxy" R units comprise the preferred R^1 , R^2 , and R^5 units. The preferred modified polyamines comprise at least 50% R^1 units that are ethylene. Preferred R^1 , R^2 , and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

- i) Substituting more preferred R^5 into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.
- ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.
- iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

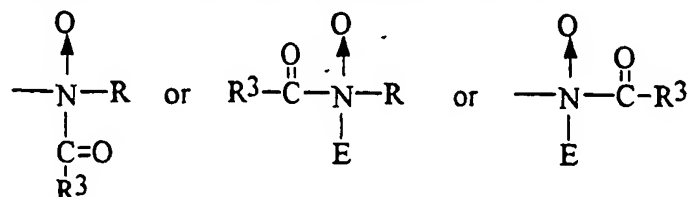
E units are selected from the group consisting of hydrogen, C_1 - C_{22} alkyl, C_3 - C_{22} alkenyl, C_7 - C_{22} arylalkyl, C_2 - C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2 - C_{22} hydroxyalkylene, benzyl, C_1 - C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According

to the present invention, the E unit $-C(O)R^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C_1 - C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q$ - $(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, preferably hydrogen, $-(CH_2)_qSO_3M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q$ - $(CHSO_2M)CH_2SO_3M$, more preferably hydrogen or $-(CH_2)_qSO_3M$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(CH_2)_pCO_2M$, and $-(CH_2)_qSO_3M$, thereby resulting in $-(CH_2)_pCO_2Na$, and $-(CH_2)_qSO_3Na$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(CH_2)_pPO_3M$ moiety substituted with sodium atoms has the formula $-(CH_2)_pPO_3Na_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate ($CH_3SO_3^-$).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; k is less than or equal to the value of n; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred modified polyamines used in the present invention comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred polyamines which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For

example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C₂-C₁₂ alkylene, preferred is C₂-C₃ alkylene, most preferred is ethylene.

The polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

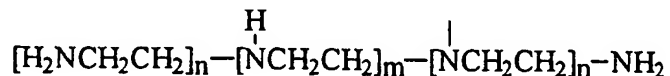
For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the modified polyamines.

Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine

(TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



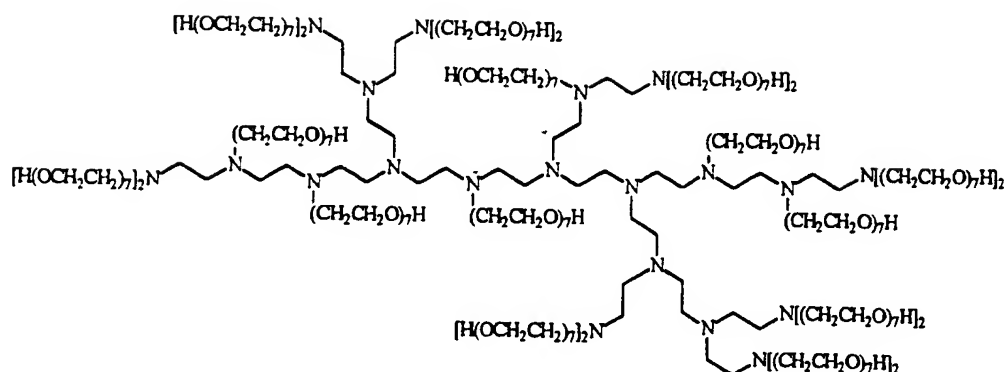
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified polyamines of the present invention comprising PEI's, are illustrated in Formulas I - IV:

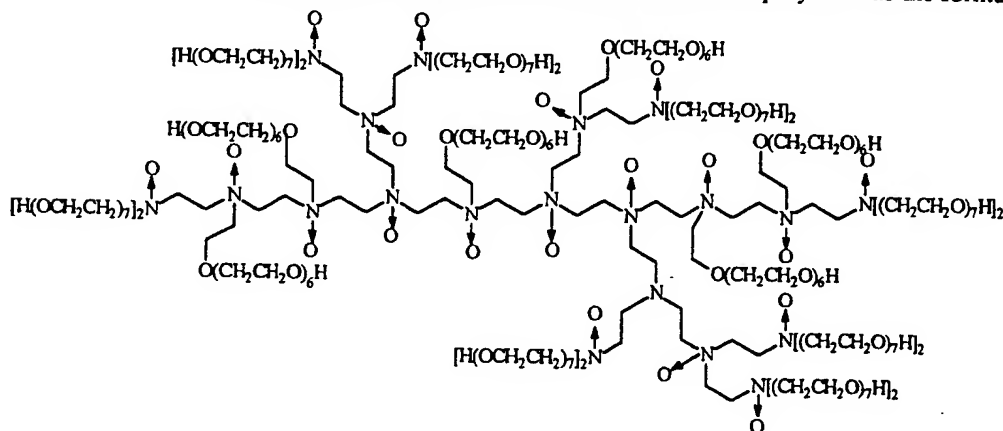
Formula I depicts a polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, - (CH₂CH₂O)₇H, having the formula



Formula I

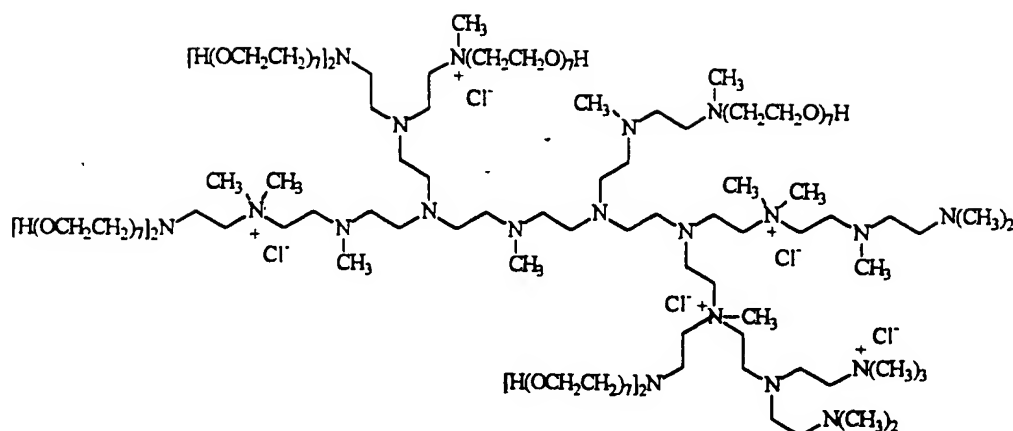
This is an example of a polymer that is fully modified by one type of moiety.

Formula II depicts a polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, wherein the polymer has the formula



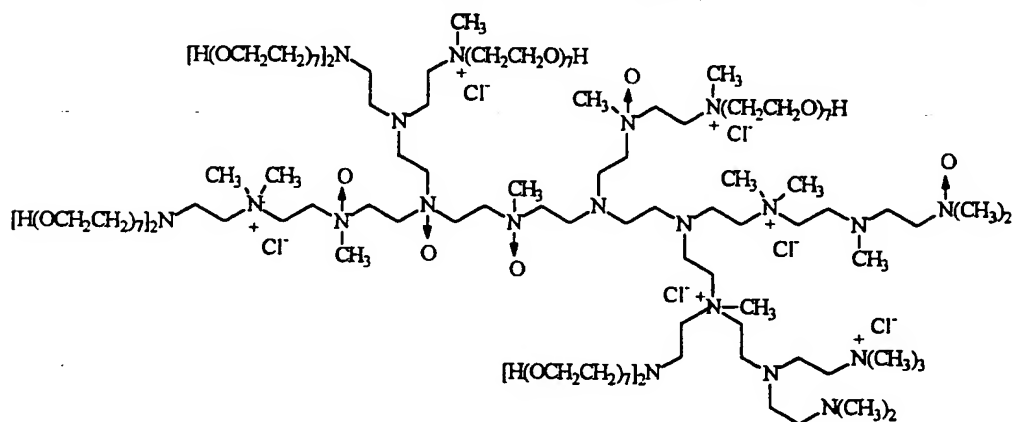
Formula II

Formula III depicts a polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(CH_2CH_2O)_7H$, or methyl groups. The modified PEI polymer has the formula



Formula III

Formula IV depicts a polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

The Anionic Agent

The anionic agent can form an ionic complex with the nitrogens of the modified polyamine. Preferably this ion complex can be formed and is stable at a pH value in the range from about 5, up to about 10. The anionic agent has anionic functionality within this pH range, whereby when mixed with the modified polyamine under conditions where the pH of the mixture is from about 5 to about 10, the anionic agent and the polyamine can complex

to form a stable, complexed polyamine. The complexation occurs at the nitrogen sites of the polyamine, where the unshared pairs of electrons are available to complex with the anionic species of the anionic agent.

Preferred anionic agents are detergent ingredients that are typically used in detergent products and which are capable of forming the anionic species within the pH range of about 5 to about 10. Nonlimiting examples of such anionic agents include anionic deterative surfactants and inorganic salts having a buffering pH of between 7 and 10, and include polyphosphate builders, such as alkali tripolyphosphate and alkali pyrophosphate. Other common detergent ingredients such as sodium carbonate and sodium silicate are generally not suitable as an anionic agent, since they either do not form a suitable anionic species at such pH, or their alkalinity is sufficiently high that solutions containing these materials have a pH generally above 10.

At a pH above about 10, the modified polyamine will resist forming any kind of an ionic complex. Therefore, when mixed with agents that have high alkalinity, or when mixed with an anionic agent of the present invention but at solution conditions where the pH is above about 10, the desired complexed polyamine will not be formed. Consequently, then the mixture is processed into a bleach detergent composition, and subsequently added into a wash solution, the uncomplexed nitrogen sites of the modified polyamine can react with and destroy the bleach agent.

Nonlimiting examples of an anionic deterative surfactant useful as an anionic agent include the conventional C_{11} - C_{18} alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C_{10} - C_{20} alkyl sulfates ("AS"), the C_{10} - C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3$ and $CH_3(CH_2)_y(CHOSO_3^-M^+)CH_2CH_3$ where x and $(y + 1)$ are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10} - C_{18} alkyl alkoxy sulfates (" AE_xS "; especially EO 1-7 ethoxy sulfates), C_{10} - C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C_{10} -18 glycerol ethers, and C_{12} - C_{18} alpha-sulfonated fatty acid esters.

Adjunct Detergent Ingredients

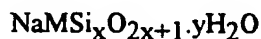
One or more adjunct detergent ingredients can be incorporated in the detergent composition during subsequent steps of the present process invention. These adjunct ingredients include other surfactants such as cationic surfactants, other detergency builders, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents such as diethylene triamine penta acetic acid (DTPA) and diethylene triamine penta(methylene phosphonic acid), smectite clays, enzymes, enzyme-stabilizing agents, dye transfer inhibitors and

perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

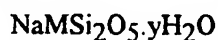
Other builders can be generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. Preferred for use herein are the phosphates, carbonates, C₁₀₋₁₈ fatty acids, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, citrate, tartrate mono- and di-succinates, and mixtures thereof (see below).

In comparison with amorphous sodium silicates, crystalline layered sodium silicates exhibit a clearly increased calcium and magnesium ion exchange capacity. In addition, the layered sodium silicates prefer magnesium ions over calcium ions, a feature necessary to insure that substantially all of the "hardness" is removed from the wash water. These crystalline layered sodium silicates, however, are generally more expensive than amorphous silicates as well as other builders. Accordingly, in order to provide an economically feasible laundry detergent, the proportion of crystalline layered sodium silicates used must be determined judiciously.

The crystalline layered sodium silicates suitable for use herein preferably have the formula



wherein M is sodium or hydrogen, x is from about 1.9 to about 4 and y is from about 0 to about 20. More preferably, the crystalline layered sodium silicate has the formula



wherein M is sodium or hydrogen, and y is from about 0 to about 20. These and other crystalline layered sodium silicates are discussed in Corkill et al, U.S. Patent No. 4,605,509, previously incorporated herein by reference.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are tetraborate decahydrate and silicates having a weight ratio of SiO₂ to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium

polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, the disclosure of which is incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylene malonic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a detergent composition. Particularly preferred polycarboxylate builders are the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

Process for Preparing Complexed Polyamines and Detergent Products therefrom

The process of the instant invention involves premixing a selected modified polyamine and an anionic agent to form the complexed polyamine. A preferred anionic agent is an anionic deterative surfactant, preferably in the form of a neutralized sulfate or sulfonate deterative surfactant paste. The surfactant paste can comprise the anionic deterative surfactant, and optionally a nonionic surfactant, but preferably will not contain a cationic

surfactant. In addition to the improved stability to bleach agents, the polyamine/surfactant complex typically has a higher oxidative degradation temperature as compared to the degradation temperature of the modified polyamines by themselves.

In a preferred process, the modified polyamine and anionic surfactant are mixed in an in-line static mixer or a conventional mixer (e.g., crutcher) for at least about 1 minute. The temperature at which the premixing step using the surfactant paste is performed typically is at a temperature of from about 25°C to about 80°C. Also, it is preferred to maintain the pH of the premix at from about 5 to about 10, more preferably at from about 8 to about 10, and most preferably at about 8 to 9. While the mixture will typically comprise only the anionic surfactant and the modified polyamine, other detergent adjuncts can be added with or to the mixture; such adjuncts can include, by example, sodium tripolyphosphate, water, and other deterative surfactants.

The modified polyamine is preferably present in an amount of from about 0.01% to about 10%, more preferably from about 0.05% to about 5%, and most preferably from about 0.1% to about 1.0%, by weight of the overall detergent composition. Further, in the premixing step, the deterative surfactant paste preferably comprises from about 1% to about 70%, more preferably from about 20% to about 60%, and most preferably from about 25% to about 50%, by weight of surfactant, and the balance water and other minor ingredients. The surfactant paste comprising the complexed polyamine can then be made into detergent products, including both granular detergent products and liquid detergent products, by processes well known to those skilled in the art.

The premixed complexed polyamine is then further processed into detergent compositions by known methods, which include slurring and spray drying, and agglomeration, as discussed herein below. The bleach detergent compositions made using the complexed polyamine, when placed into wash solutions, with or without soil loads, exhibit less loss of the bleach agent present in a washing solution compared to comparable compositions made by similar processes, except that the modified polyamine is either sprayed-on to or admixed as a particle into the detergent.

In a preferred process, the surfactant paste containing the complexed polyamine is made into a granular detergent process via a spray drying method. After the surfactant paste is processed into a detergent slurry along with other detergent adjuncts (including, by example, zeolite, inorganic salts such as sodium tripolyphosphate, carbonate and sulfate, silicates, optional detergent surfactants, polymeric polycarboxylate builders, silicates, optical brighteners, colorants, antiredeposition agents, fillers, and other compatible detergent ingredients, and mixtures thereof), the slurry is spray dried to form a spray-dried granular detergent composition. This step can be completed in a conventional spray drying tower operated at an inlet temperature range of from about 180°C to about 420°C. Such known

apparatus operates by spraying the slurry via nozzles into a counter-current (or co-current) stream of hot air which ultimately forms porous spray-dried granules.

An alternative process comprises a) premixing an anionic surfactant paste and a modified polyamine, b) agglomerating the surfactant paste comprising the complexed polyamine with other dry detergent ingredients i) initially in a high speed mixer/densifier, and ii) subsequently in a moderate speed mixer/densifier, to form agglomerates. The modified polyamine and surfactant paste are mixed for at least about 5 seconds, preferably from about 5 seconds to about 1 minute in any acceptable known mixing apparatus such as an in-line static mixer, twin-screw extruder, stirred mixing tanks and the like. The temperature at which the premixing step using the surfactant paste is performed typically is at a temperature of from about 25°C to about 80°C. The pH of the premix should be maintained between a pH of about 5 to about 10, preferably at from about 8 to about 10, and preferably without other detergent ingredients present. The modified polyamine is preferably present in an amount of from about 0.01% to about 10%, more preferably from about 0.05% to about 5%, and most preferably from about 0.1% to about 1.0%, by weight of the overall detergent composition. Further, in the premixing step, the deterative surfactant paste preferably comprises from about 1% to about 70%, more preferably from about 20% to about 60%, and most preferably from about 25% to about 50%, by weight of a deterative surfactant the balance water and other minor ingredients.

The premix of modified polyamine and surfactant paste is initially agglomerated in a high speed mixer/densifier followed by a moderate speed mixer/densifier. The high speed mixer/densifier is a Lödige CB 30 mixer or similar brand mixer. These types of mixers essentially consist of a horizontal, hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, the shaft rotates at a speed of from about 100 rpm to about 2500 rpm, more preferably from about 300 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the high speed mixer/densifier is preferably in range from about 2 seconds to about 45 seconds, and most preferably from about 5 seconds to about 15 seconds.

Preferably, the resulting detergent agglomerates formed in the high speed mixer/densifier are then fed into a lower or moderate speed mixer/densifier during which further agglomeration and densification is carried forth. This particular moderate speed mixer/densifier used in the present process should include liquid distribution and agglomeration tools so that both techniques can occur simultaneously. It is preferable to have the moderate speed mixer/densifier be, for example, a Lödige KM 600 (Ploughshare) mixer, Drais® K-T 160 mixer or similar brand mixer. The residence time in the moderate speed mixer/densifier is preferably from about 0.5 minutes to about 15 minutes, most preferably the residence time is about 1 to about 10 minutes. The liquid distribution can be accomplished

by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm. It should be understood that while the processing described herein is relative to formation of high density agglomerates, the same equipment and processing steps may be used to produce less or moderately dense agglomerates. Of course, agglomerates produced by the process regardless of the density can be admixed with less dense spray-dried granules in the final detergent product, if desired.

The detergent agglomerates produced by the process preferably have a surfactant level of from about 25% to about 55%, more preferably from about 35% to about 55% and, most preferably from about 45% to about 55%. The particle porosity of the resulting detergent agglomerates produced according to the process of the invention is preferably in a range from about 5% to about 20%, more preferably at about 10%. In addition, an attribute of dense or densified agglomerates is the relative particle size. The present process typically provides detergent agglomerates having a median particle size of from about 400 microns to about 700 microns, and more preferably from about 400 microns to about 600 microns. As used herein, the phrase "median particle size" refers to individual agglomerates and not individual particles or detergent granules. The combination of the above-referenced porosity and particle size results in agglomerates having density values of 650 g/l and higher. Alternatively, the particle size and porosity can be adjusted to produce agglomerates having lower densities, as well (e.g., 300 g/l to 500 g/l). Such features are especially useful in the production of low as well as high or conventional dosage laundry detergents as well as other granular compositions such as dishwashing compositions.

The detergent agglomerates formed by the above process are then optionally dried in a fluid bed dryer and/or further conditioned by cooling the agglomerates in a fluid bed cooler or similar apparatus as are well known in the art. Another optional process step involves adding a coating agent to improve flowability and/or minimize over agglomeration of the detergent composition in one or more of the following locations of the instant process: (1) the coating agent can be added directly after the fluid bed cooler or dryer; (2) the coating agent may be added between the fluid bed dryer and the fluid bed cooler; (3) the coating agent may be added between the fluid bed dryer and the mixer/densifier(s); and/or (4) the coating agent may be added directly to one or more of the mixer/densifiers. The coating agent is preferably selected from the group consisting of aluminosilicates, silicates, carbonates and mixtures thereof. The coating agent not only enhances the free flowability of the resulting detergent composition which is desirable by consumers in that it permits easy scooping of detergent during use, but also serves to control agglomeration by preventing or minimizing over agglomeration, especially when added directly to the mixer/densifier(s). As those skilled in the art are well aware, over agglomeration can lead to very undesirable flow properties and aesthetics of the final detergent product.

Other optional steps in the present process involve recycling oversized and undersized agglomerates as described in Capeci et al, U.S. Patent Nos. 5,489,392 and 5,516,448 (Procter & Gamble). Also, the step of including an anhydrous material at selected points in the process can be incorporated as described by Capeci et al, U.S. Patent No. 5,366,652 and 5,486,303 (Procter & Gamble). Optionally, the agglomerates exiting the moderate speed mixer/densifier can be dried in a spray drying tower as described in Capeci et al, U.S. Patent 5,496,487 (Procter & Gamble).

Optionally, the process can comprise the step of spraying an additional binder in the mixer/densifier(s). A binder is added for purposes of enhancing agglomeration by providing a "binding" or "sticking" agent for the detergent components. The binder is preferably selected from the group consisting of water, anionic surfactants, nonionic surfactants, polyethylene glycol, polyvinyl pyrrolidone polyacrylates, citric acid and mixtures thereof. Other suitable binder materials including those listed herein are described in Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble), the disclosure of which is incorporated herein by reference.

Another optional step of the instant process entails finishing the resulting detergent agglomerates by a variety of processes including spraying and/or admixing other conventional detergent ingredients. For example, the finishing step encompasses spraying on perfumes, and the addition of brighteners and enzymes to the finished agglomerates to provide a more complete detergent composition. Such techniques and ingredients are well known in the art.

EXAMPLE I

Preparation of PEI 1800 E₇

This Example illustrates a method by which one of the selected modified polyamines is made. The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave

pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE II

Formation of amine oxide of PEI 1800 E₇

This Example illustrates another method by which one of the selected modified polyamines is made. To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of about 7 ethoxy groups per nitrogen (PEI-1800, E₇) (209 g, 0.595 mole nitrogen, prepared as in Example I), and hydrogen peroxide (120 g of a 30 wt % solution in water, 1.06 mole). The flask is stopped, and after an initial exotherm the solution is stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample of the reaction mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

EXAMPLE III

Preparation of PEI 1200 E₇

This Example illustrates yet another method by which one of the selected modified polyamines is made. The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored. A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour. The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE IV

A modified polyamine is made in accordance with Example I ("PEI1800 E7") and used in the process of the current invention to form spray dried laundry granules for a bleach detergent composition. For purposes of comparison, a bleach-containing spray-dried detergent composition is made into which the PEI1800 E7 is not premixed, but is instead added after other adjunct detergent ingredients in the detergent slurry. The detergent-making process illustrated herein is executed in a conventional pilot scale system. The system contains a batch mixer (called a "crutcher") in which the premixing and slurry mixing steps are completed, followed by a conventional spray drying tower ("tower"). The PEI1800 E7 is added to the crutcher along with a sodium linear alkylbenzene sulfonate ("LAS") surfactant paste (30% LAS and balance water) and is premixed at 25°C for about 5 minutes, wherein the pH of the premix is maintained at about 8 to 10. Thereafter, silicate, optical brightener, carboxymethyl cellulose ("CMC"), sodium carbonate, and water are added to the crutcher which is then mixed. Steam at a temperature of about 120°C, sodium sulfate and sodium tripolyphosphate are added to the crutcher as the contents are continuously mixed. The crutcher is operated in a batch mode, and contains 180 kg of wet crutcher mix per batch. In the tower, the wet crutcher mix is pumped under high pressure through atomizing nozzles to form a finely divided mist. A counter-current flow of hot air (210°C) is impinged upon the atomized mist, causing the drying of the mixture ultimately resulting in spray dried granules which are collected at the exit of the tower. Continuous operation of the spray drying tower is accomplished by using an intermediate tank which accumulates multiple batches from the crutcher and feeds in a continuous manner the spray drying tower. The spray-dried granules may be further processed, by adding additional detergent ingredients, if desired, to form a fully formulated laundry detergent composition.

The following spray-dried bleach-containing granular detergent compositions are made in accordance with the process invention (i.e. Compositions Band C) and processes outside the scope of the invention (i.e. Compositions A).

<u>Composition</u>	<u>PEI1800 E7</u>	<u>PEI1800 E7</u>
	<u>Weight % in finished granules</u>	<u>Order of Addition</u>
A	1.0 %	Last wet Ingredient
B	1.0 %	Premix with LAS First
C	0.5 %	Premix with LAS First

Composition A is made via a process in which PEI1800 E7 is added as the last wet ingredient into the crutcher, without a premixing step with LAS. At this stage, the pH of the crutcher slurry is substantially higher than 10 (about 10.5-11.0). The order of addition to the crutcher is LAS paste / Silicate / Optical brightener / CMC / PEI1800 E7 / Sodium Carbonate / Water; Steam / Sodium Sulphate / Sodium Tripolyphosphate ("STPP").

Sodium tripolyphosphate and other minors are admixed to the blown powder resulting in finished granular compositions A-C for which the relative proportions of the ingredients are set forth below:

Detergent Ingredient

	<u>A</u>	<u>B</u>	<u>C</u>
LAS	18.0	18.0	18.0
PEI1800 E7	1.0	1.0	0.5
Bleach agent *	4.0	4.0	4.0
Sodium silicate (2.0R)	5.8	5.8	5.8
Optical brightener**	0.2	0.2	0.2
CMC	0.3	0.3	0.3
Sodium carbonate	10.0	10.0	10.0
Sodium sulfate	31.9	31.9	32.4
STPP	22.0	22.0	22.0
Water and minors	<u>6.8</u>	<u>6.8</u>	<u>6.8</u>
	100.0	100.0	100.0

* The bleach agent is a 2:1 weight ratio of sodium perborate monohydrate and sodium nonanoyloxybenzene sulfonate bleach activator.

** Optical brightener slurried in 0.2% C45E7 Nonionic to ensure presence in organic phase.

The bleach detergent compositions B and C, made by premixing the PEI1800 E7 with LAS, exhibits less loss of the bleach agent in a wash solution compared to composition A made by same process, except wherein the PEI1800 E7 is the last wet ingredient added to the slurry.

EXAMPLE V

A modified polyamine is made in accordance with Example I ("PEI1800 E7") and used in the process of the current invention to form an agglomerated detergent composition. An in-line static mixer is used into which the PEI1800 E7 is added continuously along with a sodium linear alkylbenzene sulfonate ("LAS") surfactant paste (60% LAS and balance water) at about 60°C in order to completely mix the ingredients, wherein the pH of the premix is maintained at about 7 to 10. Thereafter, the premix are continuously fed to a high speed mixer/densifier (Lödige CB-30, commercially available from Lödige) along with sodium aluminosilicate (zeolite) and sodium carbonate. The rotational speed of the shaft in the Lödige CB-30 mixer/densifier is about 1400 rpm and the mean residence time is about 10 seconds. The contents from the Lödige CB-30 mixer/densifier are continuously fed into a Lödige KM 600 mixer/densifier for further agglomeration during which the mean residence time is about 6 minutes. The detergent agglomerates are then screened with conventional screening apparatus

resulting in a uniform particle size distribution. A bleach agent is then admixed with the detergent agglomerates to form the bleach detergent product, having the set forth below:

<u>Component</u>	<u>% Weight</u>
C ₁₂₋₁₃ linear alkylbenzene sulfonate	27.1
Sodium aluminosilicate	34.4
Sodium carbonate	17.5
Polyethylene glycol (MW 4000)	1.3
PEI1800 E7	1.0
Bleach agent *	3.0
Misc. (water, etc.)	<u>15.7</u>
	100.0

** The bleach agent is a 2:1 weight ratio of sodium perborate monohydrate and sodium nonanoyloxybenzene sulfonate bleach activator.

The agglomerated detergent composition made by premixing the PEI1800 E7 with LAS in the premixer exhibits less loss of the bleach agent in a wash solution, compared to a composition made by same process, except wherein the PEI1800 E7 is sprayed-on to the detergent agglomerates after agglomeration.

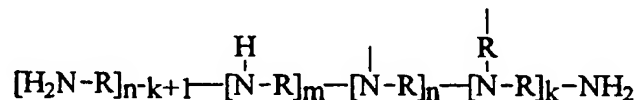
Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. A bleach detergent composition comprising:
 - a) a bleach agent, and
 - b) a complexed polyamine, comprising
 - i) a modified polyamine useful as a cotton soil release and dispersant agent, and
 - ii) an anionic species capable of forming a complex with the modified polyamine.
2. The bleach detergent composition according to Claim 1 wherein the modified polyamine has a polyamine backbone corresponding to the formula:



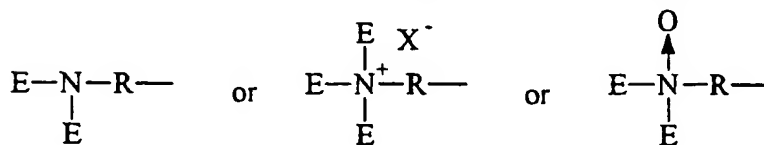
having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:



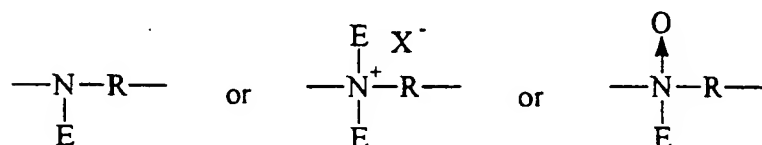
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$,

wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

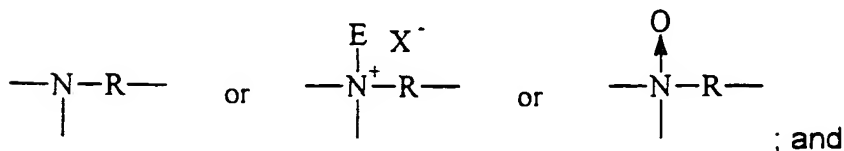
- i) V units are terminal units having the formula:



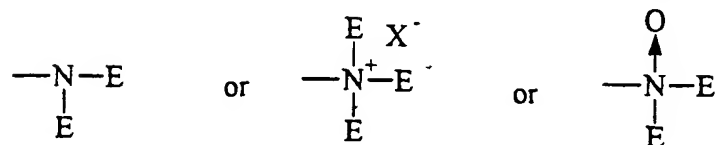
- ii) W units are backbone units having the formula:



- iii) Y units are branching units having the formula:



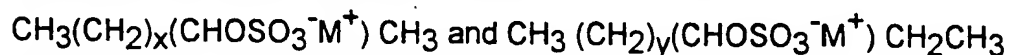
iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OR²)CH₂-, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R¹O)_xB, -C(O)R³, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

3. The bleach detergent composition according to Claim 2 wherein the anionic agent is selected from an anionic deterative surfactant, and inorganic salt having a buffering pH of between 7 and 10, and mixtures thereof.

4. The bleach detergent composition according to Claim 3 wherein the anionic agent is an anionic deterative surfactant selected from the group consisting of C₁₁-C₁₈ alkyl benzene sulfonate, C₁₀-C₂₀ alkyl sulfate, C₁₀-C₁₈ secondary (2,3) alkyl sulfate of the formula



where x and (y + 1) are integers of at least about 7, and M is a water-solubilizing cation, especially sodium, alkenyl sulfate, C₁₀-C₁₈ alkyl alkoxy sulfate, C₁₀-C₁₈ alkyl alkoxy carboxylate, C₁₀-18 glycerol ether, C₁₂-C₁₈ alpha-sulfonated fatty acid ester, and mixtures thereof.

5. The bleach detergent composition of Claim 2 wherein the bleach agent is selected from the group consisting of sodium perborate tetrahydrate, sodium perborate monohydrate, sodium percarbonate, and mixtures thereof.

6. The bleach detergent composition according to Claim 5 further comprising a bleach activator which can combine with a peroxygen bleaching agents *in situ* in an aqueous solution to form a peroxy acid bleaching agent corresponding to the bleach activator.

7. The bleach detergent composition according to Claim 6 wherein the bleach activator is selected from nonanoyloxybenzene sulfonate, tetraacetyl ethylene diamine, and mixtures thereof.

8. A bleach detergent composition comprising:

- a) from about 0.1% to about 30% by weight a deterative surfactant selected from the group consisting of anionic, nonionic, cationic, zwitterionic, and ampholytic surfactants, and mixtures thereof;
- b) from about 0.5% to about 30% by weight a bleach agent;

- c) from about 0.01 to about 10% by weight a complexed polyamine comprising a water-soluble alkoxylated polyamine and an anionic deterative surfactant; and
- d) adjunct ingredients selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer agents, dispersants, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

9. A process for preparing a bleach detergent composition comprising the steps of:

- a) premixing a modified polyamine which is useful as a cotton soil release and dispersant agent, with an anionic agent capable of forming a complex with the modified polyamine, to form a complexed polyamine;
- b) combining the premix with other detergent ingredients; and
- c) adding to the combination a bleach agent.

10. The process according to Claim 9 wherein the anionic agent is an anionic deterative surfactant, in the form of a surfactant paste.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/02394

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/39 C11D3/37 C11D1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 42285 A (GOSSELINK EUGENE PAUL ;WATSON RANDALL ALAN (US); MANOHAR SANJEEV K) 13 November 1997 see example 15 see claims 1-3 see page 29, line 31 - line 34 ---	1-8
E	WO 99 07816 A (UNILEVER PLC ;UNILEVER NV (NL)) 18 February 1999 see page 9, line 25 - line 29 see Formulations 1,2 see claims 1-6 ---	1-8
A	WO 97 42294 A (PANANDIKER RAJAN KESHAV ;GHOSH CHANCHAL KUMAR (US); PROCTER & GAMB) 13 November 1997 see page 29, line 12 - page 30, line 20 see claims 1,2,13,15 ---	1-8
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

1 June 1999

Date of mailing of the international search report

14/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/02394

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 42293 A (PROCTER & GAMBLE) 13 November 1997 see page 39, line 5 - page 43, line 27 see claims 1-3	1-8
P,A	EP 0 839 903 A (PROCTER & GAMBLE) 6 May 1998 see page 3, line 15 - page 4, line 32 see page 5, line 21 - line 43 see page 21, line 1 - line 26	1,2,4,5, 8
P,A	WO 98 08928 A (LICKISS JAMES ROBERT ;WATSON ALAN RANDALL (US); CHAPMAN BENJAMIN E) 5 March 1998 see claims 1-10	9,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/02394

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9742285 A	13-11-1997	AU 2811097 A	26-11-1997
		CA 2252859 A	13-11-1997
		EP 0917562 A	26-05-1999
		NO 985106 A	04-01-1999
WO 9907816 A	18-02-1999	AU 9258598 A	01-03-1999
WO 9742294 A	13-11-1997	AU 2743497 A	26-11-1997
		AU 2815097 A	26-11-1997
		CA 2252852 A	13-11-1997
		CA 2252853 A	13-11-1997
		CZ 9803548 A	17-03-1999
		EP 0910618 A	28-04-1999
		NO 985103 A	04-01-1999
		WO 9742287 A	13-11-1997
WO 9742293 A	13-11-1997	AU 2743497 A	26-11-1997
		CA 2252852 A	13-11-1997
		CA 2252861 A	13-11-1997
		EP 0907704 A	14-04-1999
		WO 9742287 A	13-11-1997
EP 0839903 A	06-05-1998	AU 5168698 A	22-05-1998
		WO 9818893 A	07-05-1998
WO 9808928 A	05-03-1998	NONE	

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)